California Environmental Protection Agency

Air Resources Board

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

MLD SOP SAS05

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF EXEMPT COMPOUNDS IN AEROSOL CONSUMER PRODUCT PROPELLANT BY GAS CHROMATOGRAPHY

October 17, 2003, Revision 2.1

DISCLAIMER: Mention of any trade name or commercial product in Method 310 and associated Standard Operating Procedures does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

1 INTRODUCTION

This document describes a procedure for the analysis of aerosol consumer product propellants containing "exempt" compounds as identified under Title 17, California Code of Regulations, Division 3, Chapter 1, Subchapter 8.5, Articles 1 and 2, Sections 94500-94517. Under the regulations, the following gaseous compounds are exempt from the definition of "Volatile Organic Compounds (VOC): carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), 1,1-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a), trifluoromethane (HFC-23), and 1,1,1,2-tetrafluoroethane (HFC-134a). At this time, it is expected that only HFC -152a, HFC -134a, CO_2 and nitrogen (N_2) will be used in products. For more information see ARB Method 310, U.S. EPA Method 18, U.S. EPA Method 8240, ASTM D 859-88 and NIOSH 1400.

2 SUMMARY OF METHOD

This procedure analyzes the propellant portion of an aerosol sample. An aerosol container is pierced and the propellant is collected in a one-liter evacuated Tedlar bag. This aliquot is injected into a gas chromatograph with thermal conductivity detector (GC/TCD) and the components of the propellant are then identified. Any exempt compounds present are quantified. The data produced from the GC/TCD are in volume based units, therefore density measurement is needed to convert the data into a mass based format.

3 INTERFERENCES/LIMITATIONS

3.1 The aerosol propellants will be one or a combination of CO_2, fluorocarbons, propane, dimethyl ether (DME), isobutane, and butane. The expected retention times of these propellants are listed in Table 1. HFC-152a and HFC-134a are not fully resolved in the screening method, however, they are not likely to be present together as a propellant mixture.

3.2 Unless care is taken to completely evacuate the propellant collection system and sweep out any connecting lines to the bag with product before starting collection, nitrogen may be detected in the bag contents. As long as the nitrogen contamination is less than 0.1% by weight of the sample, this contamination will not affect the results of the analysis.

3.3 Components with similar retention times to the analytes will interfere in this procedure.

3.4 Analysis of the propellant sample should be completed within three days. Tedlar bags are semi-permeable thus the longer the bags sit before analysis, the more likely the presence of nitrogen. For each analysis, fresh bags of helium blank, check and standard should be prepared.

4 APPARATUS AND MATERIALS

4.1 Balance, capable of accurately weighing to 0.01 g.

4.2 Can Piercing Platform (Figure 1)

4.3 Density Meter, Mettler-Toledo DE 50.

4.4 Gas Chromatograph (GC), Varian 3800 equipped with TCD with a 16 position modified stream selector for automated analysis using STAR workstation.

4.4.1 GC Capillary Column, 30 m x 0.53 mm ID Restek RT Q- PLOT column.

4.4.2 GC system working parameters:

Injector Temperature	120°C
Detector Temperature	240°C

Oven Temperature Program:

Initial:	40°C for 3.0 min.
Rate:	20°C/min to 220°C
Hold time:	4.0 min
Column Flow Rate:	7 ml/min
TCD Reference Flow:	15 ml/min
Split Vent Flow:	40 ml/min

4.5 Platform Shaker, Thermolyne M49125

4.6 Propellant Collection System (Figure 2), with house vacuum

4.7 Refrigerator, capable of maintaining temperature above 0°C and below 10°C

4.8 Tedlar Bags, 1 liter, equipped with slip valve and septum

4.9 Vial, 40 mL, amber, with septa cap, for archival sampling

4.10 Vial, 20 mL, clear, with septa cap, for working sample aliquot

5 GASES AND REAGENTS

5.1 Helium, Grade 5

5.2 HFC-152a, 98%

5.3 HFC-134a, 98%
5.4 Screen Standard #1, 33% v/v mixture of HFC-134a, HFC-152a and CO_2

5.5 Screen Standard #2, 25% v/v mixture of propane, dimethyl ether, isobutane, and butane

6 PROCEDURE

6.1 Propellant Collection (see Appendix A)

6.1.1 Prepare Tedlar bags.

6.1.2 Position aerosol sample in the Can-Piercing Platform.

6.1.3 Begin venting aerosol sample using the Propellant Collection System.

6.1.4 After flow of propellant is established, fill Tedlar bag to obtain propellant sample.

6.2 Propellant Analysis (see Appendix B).

6.2.1 Attach and open sample Tedlar bag to GC autosampler.

6.2.2 Perform screen analysis, to determine the composition of the propellant.

6.2.3 For any samples containing either HFC-152a or HFC-134a, perform quantitative analysis using the pure compound. If CO_2 is present, it is given a 100%.

6.3 Density Measurement (see Appendix C).

6.3.1 If an exempt propellant is present, the density is determined from the same Tedlar bag on density meter. The value is used to calculate the grams of exempt propellant found in the product.

7 CALCULATIONS

7.1 The Total Grams Exempt VOC in the propellant is calculated as follows (assuming 25°C):

$$\text{Exempt Propellant, } \frac{\text{grams}}{\text{L}} = \left(\frac{\text{Molecular Weight of Exempt, grams}}{24.5\,\text{L}} \right) \times \left(\text{Exempt Propellant, v/v} \right)$$

Then,

$$\text{Exempt Propellant, grams} = \left(\text{Exempt Propellant, } \frac{\text{grams}}{\text{L}} \right) \times \left(\frac{\text{Propellant, grams}}{\left(\text{Propellant Density, } \frac{\text{grams}}{\text{mL}} \times \frac{1000\,\text{mL}}{\text{L}} \right)} \right)$$

Table 1

COMPOUND RETENTION TIMES

COMPOUND	RETENTION TIME (minutes)
Nitrogen	2.6
Carbon Dioxide	3.2
HFC-134a	7.1
HFC-152a	7.3
Propane	8.1
Dimethyl Ether	8.7
Isobutane	10.2
n-Butane	10.8

Figure 1
Can-Piercing Platform

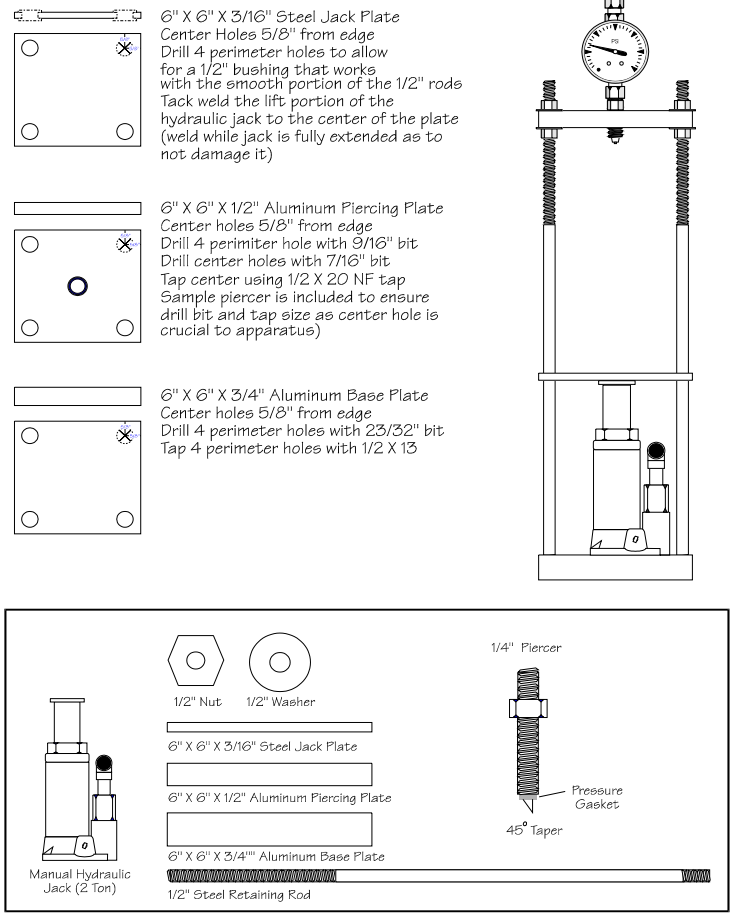
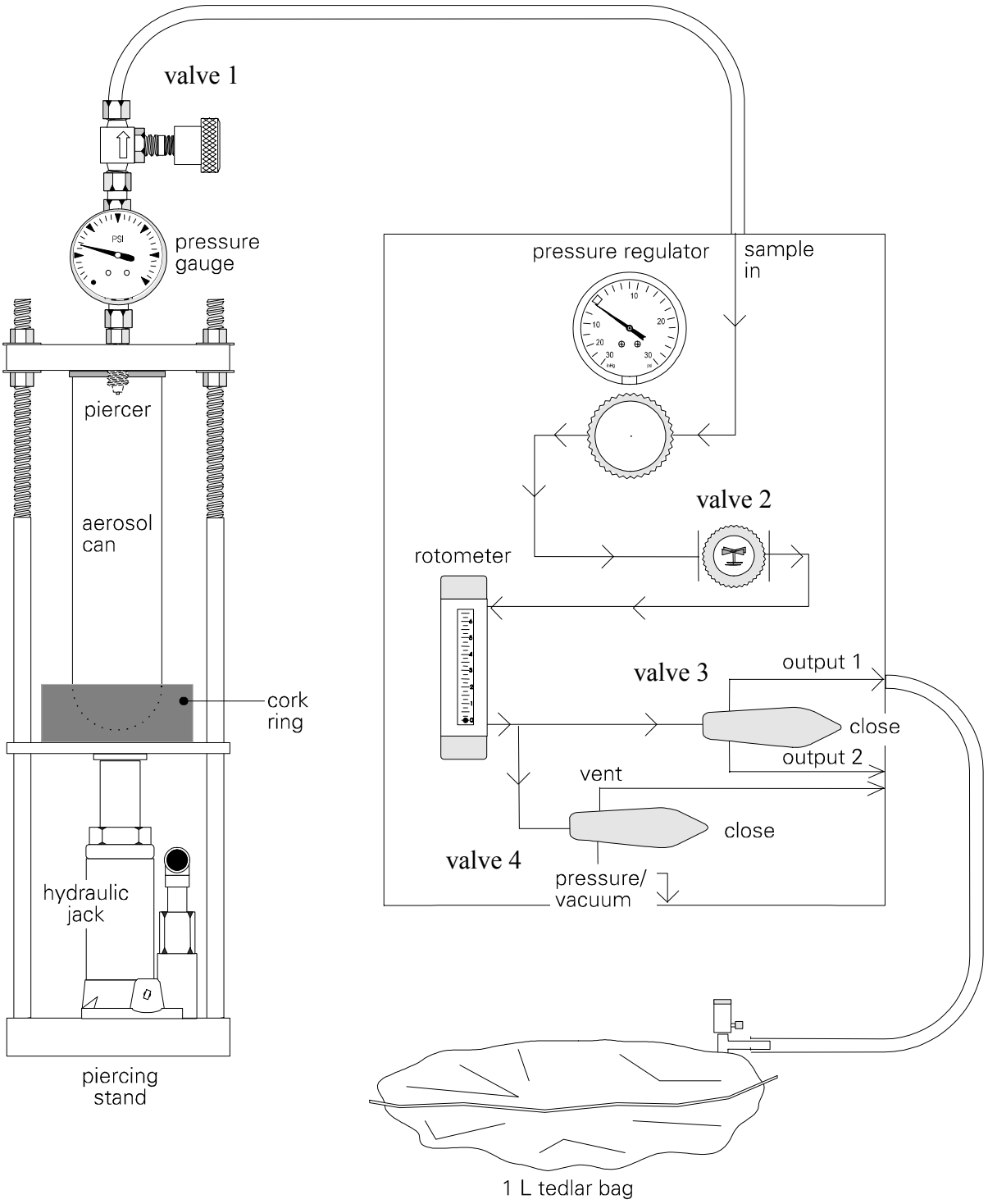


Figure 2
Propellant Collection System



APPENDIX A

Collection of Propellant from Aerosol Consumer Products

1. Evacuate Tedlar Bag: Turn Valve #3 to Output #1, attach the sample Tedlar bag and open the valve 1.5 turns. Fully evacuate the bag using vacuum and then fill the bag with helium. Repeat three times to fully "flush" the bag. Close the valve on the bag and disconnect.

2. Close Valves 1 – 4 on the Propellant Collection System.

3. Weigh sample can (that has been stored in a refrigerator, upside down) to the nearest 0.01 g. Record this as the "full can" weight.

4. Center sample can, top side down, onto the cork ring of the sample piercing platform.

5. Check that the hydraulic jack valve is closed.

6. Slowly raise the jack until the can is pierced. Note the pressure of the can on the pressure gauge. (If the can pressure is decreasing, a good seal has not been achieved, raise the jack an additional 2-3 mm until the gauge stabilizes.)

7. Open Valve 1 to pressurize the system.

8. Open Valve 3 and Valve 2, sequentially.

9. Slowly turn the pressure regulator knob until constant flow is established on the rotometer. Some slight adjustment may be necessary to maintain the initial flow.

10. When propellant vapor is visible from Output 1 attach the Tedlar bag, open the bag valve 1.5 turns and collect the propellant.

11. When Tedlar bag is full, close the bag valve and disconnect. The Tedlar bag is now ready for GC analysis (see Appendix B & C).

12. Open Valve 4 to the vent position.

13. Periodic adjustments to the pressure regulator knob will be necessary, until it is in the full open positions.

14. When the pressure gauge indicates zero pressure and the rotometer is no longer indicating flow, the can is fully vented.

15. Turn the hydraulic jack valve open, and carefully lower the sample can. Close the hydraulic jack valve.

16. Remove the sample can and transfer it to the platform shaker. Set platform shaker between 100 – 150 rpm and allow the can to set overnight.

17. Remove the sample can from the platform shaker. Weigh sample can, to the nearest 0.01 g. Record this as the “vented can” weight.

18. Open sample can. Mix and transfer liquid sample to both a 20 mL and 40 mL vial.

19. Properly dispose of any remaining liquid sample.

20. Rinse can to remove any residues. Allow the can to dry completely.

21. Weigh sample can, to the nearest 0.01 g. Record this as the “empty can” weight.

APPENDIX B

Propellant Analysis

1. Attach each Tedlar bag sample to a port on the GC autosampler manifold. Make certain you snug the nuts and turn the bag valve 1.5 turns.

Screen Method - run each time

The SCREEN method is used to take a qualitative look at each propellant sample.

2. Loading Method: On the toolbar of the System Control panel there is an icon showing the currently loaded method. To the right is a folder, click on this to load and activate SCREEN method.

3. Sample Sequence: Under File, click on Open Sample List. Click on Screen.smp, then Open. The first five lines stay constant to initialize the program, run the helium blanks and the screen standards. Starting on line six, each sample bag is assigned a stream number, corresponding to the port of attachment. The loop size for this entire analysis is "01". The last line of the sequence is set up to put instrument on STANDBY.

4. Data files: At the bottom of the sample sequence window, click on Data Files. A new screen will come up, double click on [current year] data. Click on New Folder and enter the date (e.g. mmddyy.), then click OK. Click OK, again.

5. Printing Sequence: Under File, click on Print. Verify information and data file destination. The directory file should read: *c:\star\data\[current year] data\mmddyy*. If the path is not reading this, then go back in to explorer and delete the file and start again. Place sample sequence in the instrument logbook.

6. Start Analysis: Click Begin at the bottom of the sample sequence window. Verify the correct method is indicated.

7. After the completion of the run, review the data, and if any sample contains exempted compounds then continue on to step 8 for the quantitative analysis for that specific compound.

Quanitative Analysis - as required

If an exempt propellant is identified, then that sample will be run using the method and standards specific for the compound of interest (HFC-152a is the most commonly found exempted propellant). An Instrument Check, pure sample of the specific compound being quantified, is run to verify that the calibration ran correctly. A Sample Check, Screen Standard #1, ensures the sampling of the Tedlar bags.

8. Loading Method: On the toolbar of the System Control panel there is an icon showing the currently loaded method. To the right is a folder, click on this to load and activate 152A method.

9. Sample Sequence: Under File, click on Open Sample List. Click on 152a.smp, then Open. The first nine lines stay constant to initialize the program, run the helium blanks and run a five-point calibration. Line ten is an Instrument Check which verifies the operation of the instrument loops (loop "04"). Line eleven is the Sample Check which runs Standard #1 through the sample loop, "05". Starting on line twelve, each sample bag is assigned a stream number, corresponding to the port of attachment. The loop size for this entire analysis is "05". The last four lines of the sequence repeat, in order, Sample Check, Instrument Check, helium blank. The last line of the sequence is set up to put instrument on STANDBY.

10. Data files: At the bottom of the sample sequence window, click on Data Files. A new screen will come up, double click on [current year] data. Click on New Folder and enter the date (e.g. mmddyy.), then click OK. Click OK, again.

11. Printing Sequence: Under File, click on Print. Verify information and data file destination. The directory file should read: *c:\star\data\[current year]* data\mmddyy. If the path is not reading this, then go back in to explorer and delete the file and start again. Place sample sequence in the instrument logbook.

12. Start Analysis: Click Begin at the bottom of the sample sequence window. Verify the correct method is indicated.

13. After the completion of the run, review the data.

14. Close and remove all sample bags.

15. Attach and snug up plugs on the GC autosampler manifold ports.

APPENDIX C

Propellant Density Analysis

The Consumer Products Regulation requires data be reported in a mass-based format. Since the GC propellant data is volume based, a density measurement is necessary for the conversion.

Calibration – monthly

Inspect the desiccant in the cartridge on top of the instrument to make sure it is adequate for analysis. Change as necessary.

1. Remove purge line from the deionized water trap and dry it thoroughly. This may require blowing "Techspray" through the line. Place it into the desiccant port labeled "DP" on right side of instrument.

2. Press PUMP, allowing dry air to fill the measuring cell.

3. Press CALIBRATE.

4. Press ENTER when the instrument calls for "Purge Ok?" (ρ_{air} = 0.00116-0.00124)

5. When instrument calls for "water" remove clear intake tubing from the lower intake port. Remove the purge tubing from the desiccant port and place it into the deionized water trap, with the end below the surface of the water.

6. Inject approximately 3 mL of Nanopure water (or Mettler Standardized water) into the lower intake port, making sure that the water passes through the measuring cell and out the purge line. Do not remove the syringe.

7. Press ENTER.

8. The instrument will complete the calibration and print out a report. If calibration is successful, record value and press RESET. If unsuccessful, repeat steps 1 through 9.

9. Record value in instrument lab book.

10. Inject 3 mL of acetone followed by several syringes full of air to completely dry the measuring cell. Inspect that all droplets of liquid are gone before proceeding to next step. If necessary blow "Techspray" gently through the cell and purge line tubing.

11. Remove purge line from the deionized water trap and dry it thoroughly. Use "Techspray" to dry purge line if necessary. It is important to have all traces of water removed from the purge line. Place it into the desiccant port (DP).

12. Press PUMP, allowing air to dry the measuring cell. Press PUMP again to shut off.

13. Replace purge line to the deionized water trap. Replace clear intake tubing in the lower intake port.

Sampling - for every batch of sample

Instrument Check

Helium is used for check; expected ρ_{He} = 0.00018.

14. Attach helium Tedlar bag, opening valve at least one turn. Purge dry measuring cell with Helium prior to actual measurement by gently pressing on Tedlar bag.

15. Press CHECK.

16. Lightly press the Tedlar bag to introduce gas into the measuring cell, noting a steady stream of bubbles in the deionized water trap. Close Tedlar bag, leaving it attached.

17. Press ENTER.

18. The instrument will complete the check and print out a report. The instrument will pass/fail based on $\pm$ 0.00002.

19. Record value in instrument lab book.

20. Press RESET, and disconnect Tedlar bag.

Sample Check

Hydrofluorocarbon-152a is used for the sample check; expected ρ_{152a} = 0.00270-0.00278.

21. Attach 152a Tedlar bag, opening bag valve at least one turn.

22. Lightly press the Tedlar bag to introduce gas into the measuring cell, noting a steady stream of bubbles in the deionized water trap. Close Tedlar bag, leaving it attached.

23. Press MEASURE.

24. The instrument will complete the measurement and print out a report. Record value in instrument lab book.

25. Press RESET.

Samples

26. The instrument is ready to run samples.

27. Attach sample Tedlar bag, opening bag valve at least one turn.

28. Repeat steps 22 through 25 until all samples are tested.

29. The instrument check (He) and sample check (152a) are run again after the last sample by repeating steps 14 through 25.

SOP Revision History

DATE	VERSION	NOTES
October 16, 1996	1.0	Analysis is by an initial screening method for the presence of R-152a or R-134a. If present a four-point calibration is made and the samples reanalyzed. The oven temperature and run time has been extended to remove propellants like isobutane and dimethyl ether from the column to minimize interference. Carbon dioxide, if present, will be 100% and given full exemption.
March 10, 1998	1.1	Adjusted document font to Times New Roman 12. Inserted Appendix A and B formerly a stand-alone document.
December 10, 1999	2.0	The analysis is now on a Varian 3800, with valve controllers and the Star software system. The column is a Restek Q-PLOT megabore. Included is the SOP for the Mettler density determination, Appendix C.
October 17, 2003	2.1	SOP updated to reflect the various modifications made to the propellant analysis. Changes include optimizing GC analysis, including a five-point calibration and clarifying the calculation equation. Additional changes include font (Arial 12) conversion, grammar and nomenclature corrections, enumeration correction.